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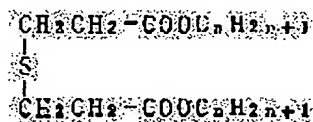
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(54) PRIMARILY EXPANDED POLYSTYRENE PARTICLE EXCELLENT IN MOLDABILITY AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain an expanded particle, containing a specific foam regulator and a readily volatile foaming agent in respective small proportions in polystyrene, primarily expanded to a specific bulk ratio and a specified average cell diameter without using an organic solvent, etc., and causing mutual coalescence thereof.

CONSTITUTION: This particle is obtained by comprising 0.001-0.01 pt.wt. foam regulator expressed by the formula $[(n) \text{ is } 10-20]$ and 0.056-0.16mol% readily volatile foaming agent (preferably having -30 to $+50^{\circ}\text{C}$ boiling point, e.g. butane, pentane, monochlorodifluoroethane or tetrafluoroethane) in 100 pts.wt. polystyrene and then expanding the resultant mixture under $0.4-1.5\text{kg/cm}^2$ gauge vapor pressure. The resultant particle has 100-300 times bulk ratio and 0.05-0.3mm average cell diameter.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the polystyrene primary foaming particle which has the moldability which ***** foamed 100 to 300 times highly, and was excellent in them, and its manufacture approach.

[0002]

[The conventional technique and a trouble] A polystyrene foaming object uses the expandable polystyrene particle containing a foaming agent as a raw material, heats this, obtains a primary foaming particle, subsequently to in a die is filled up with it, and is acquired as a foaming object with a desired configuration by heating with a steam etc. Conventionally, although several to about about 80 times thing is suitably used for expansion ratio according to the application, in the field of a buffer packing material, a heat insulator, float material, the cut article of a block, etc., as for this foaming object, the thing of high expansion ratio has been required more recently. In order to acquire the Plastic solid formed into high foaming, even if it carries out foaming using the primary foaming particle which only merely gathered primary expansion ratio, only what has the low welding reinforcement between each particle is obtained greatly [contraction] by the acquired Plastic solid.

[0003] There is a technique which uses the styrene acrylonitrile system resin which is one of the styrene resin, and which is easy to make it form into high foaming to want of these high-expansion-ratio-foaming objects. however, these styrene acrylonitrile system resin product while saving-resources-izing and recycle utilization are promoted — a polystyrene product and most exteriors — distinction is impossible and it was easy to mix up an operator, and when collecting polystyrene, there was a problem in which styrene acrylonitrile system resin is mixed. Thus, since utility value is almost lost, as for want of the high-expansion-ratio-foaming object of polystyrene, the recovery raw material with which polystyrene and styrene acrylonitrile system resin were mixed has a still strong thing.

[0004] As an approach of obtaining a polystyrene system resin high foaming particle, carry out the amount activity of specification of the specific foaming agent, JP,61-195135,A is made to foam to altitude once, and the method of obtaining a styrene resin high foaming particle is indicated by carrying out the spontaneous recovery of the foaming particle contracted after that. By this approach, the styrene resin foam particle by which high foaming was carried out shall be obtained 100 to 300 times. Moreover, while a clearance etc. can be filled up with the foam particle obtained by this approach as it is and it can be used as shock absorbing material and a heat insulator, the homopolymer of polystyrene, i.e., polystyrene, is received. When a well-known cellular regulator, for example, talc etc., was used conventionally, even if it carried out foaming, only what has the low welding reinforcement between each particle was obtained greatly [contraction] by that air bubbles become fine too much and it is hard to go up expansion ratio and the acquired Plastic solid.

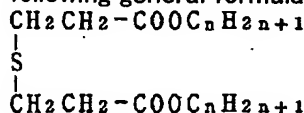
[0005] Moreover, as an approach for acquiring the high-expansion-ratio-foaming object of polystyrene, to JP,63-182353,A, use together a specific foaming agent and a specific organic solvent, make it foam for a high scale factor primarily, it is made to recover the thing which carried out post shrinkage, and the method of carrying out late-coming bubble shaping and acquiring a polystyrene high-expansion-ratio-foaming object is indicated. However, by this approach, while it becomes possible easily to make polystyrene form into high foaming by using an organic solvent, it is easy to produce the phenomenon which foaming particles fuse in the case of primary foaming, and when especially vapor pressure is raised and it foams to it primarily,

this phenomenon tends to happen. The primary foaming particle in which these coalescent particles were contained does not fully carry out contraction recovery after primary foaming, therefore cannot do good foaming. Moreover, when it was used as shock absorbing material, there was a possibility of producing the problem that this organic solvent shifts to packaging goods-ed.

[0006] In view of such the actual condition, this invention persons do not make fusion etc. start, but get efficiently the polystyrene foaming particle made to foam 100 to 300 times primarily. And in case the obtained foaming particle makes expansion ratio foam 100 to 300 times primarily as a result of inquiring wholeheartedly so that it may become the thing excellent in the moldability, so that it may become the range of specification [the diameter of air bubbles of foam] By adjusting the foaming agent and the specific cellular regulator of the amount of specification to the specific range, using them together, and foaming primarily with the vapor pressure of specific conditions It can foam to altitude, without using additives, such as an organic solvent, and the primary foaming particle which demonstrates the outstanding moldability is obtained, and the obtained primary foaming particle finds out carrying out contraction recovery to ***** before contraction mostly by carrying out natural neglect, and comes to complete this invention.

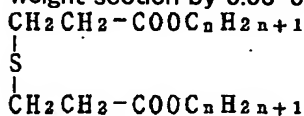
[0007]

[Means for Solving the Problem] That is, this invention is a compound [** 3] shown by the following general formula (1) to the polystyrene 100 weight section.



(但し、 $20 \geq n \geq 10$ とする。)

The compound in which the 0.001 - 0.01 weight section and 0.056-0.16 mol % of easy-volatility foaming agents are contained, and the ***** is shown in an easy-volatility foaming agent to 100 to 300 times, the polystyrene primary foaming particle which was excellent in the moldability characterized by the diameter of average air bubbles being 0.05-0.3mm, and the polystyrene 100 weight section by 0.08-0.16-mol % and the following general formula (1) [** 4]



(但し、 $20 \geq n \geq 10$ とする。)

It is the expandable polystyrene particle which carried out 0.001-0.01 weight section content, and was subsequently obtained at gage pressure 0.4kg/cm² Above, 1.5kg/cm² It is characterized by foaming using the steam under pressure of the following. Let the manufacture approach of a polystyrene primary foaming particle that contained said compound 0.001 - 0.01 weight sections, and 0.056-0.16 mol % of easy-volatility foaming agents, and the moldability 100 to 300 times and whose diameter of average air bubbles are 0.05-0.3mm was excellent in ***** be a summary.

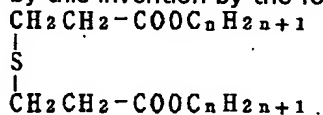
[0008] The polystyrene used in this invention may be the homopolymer of a styrene monomer, and polymerization methods may be any of the approach of carrying out a suspension polymerization from a styrene monomer, and the approach by the nucleus polymerization. Moreover, if initial-complement addition of the cellular regulator is carried out at the time of these polymerizations, the polystyrene particle which made homogeneity contain a cellular regulator can be obtained.

[0009] The easy-volatility foaming agent contained in polystyrene in this invention is independent, or mixes aliphatic hydrocarbon or two or more sorts of halogenated hydrocarbon. As an example of aliphatic hydrocarbon, a propane, n-butane, an isobutane, n pentane, an isopentane, a cyclopentane, etc. are mentioned. Moreover, trichloromonofluoromethane, a dichlorodifluoromethane, monochlorotrifluoromethane, dichloromonofluoromethane,

monochlorodifluoromethane, trichlorofluoroethane, the dichlorotetrafluoroethane, dichlorotrifluoroethane, monochloropentafluoroethane, monochlorotetra fluoroethane, monochlorotrifluoro ethane, monochlorodifluoroethane, tetrafluoro ethane, difluoroethane, etc. are mentioned as an example of halogenated hydrocarbon. Especially, a boiling point-30-50 degree C foaming agent, for example, butane, a pentane, monochlorodifluoroethane, tetrafluoro ethane, etc. are [that it is especially easy to obtain the foam of a high scale factor] desirable.

[0010] The expandable-polystyrene particle used by this invention can fuse polystyrene using the suspension impregnation method which sinks in an easy-volatility foaming agent in aqueous suspension, and an extruder, can press fit and knead an easy-volatility foaming agent, and can use for and acquire the well-known approach of the extrusion impregnation method which it quenches bywater and is cut from the nozzle which carried out the desired configuration with discharge and the condition of not foaming. After making polystyrene contain a foaming agent by these approaches and riping in dehydration, desiccation, and a cool place, the amount of foaming agents contained in the expandable polystyrene particle at the time of foaming primarily needs to be 0.08-0.16-mol % to the polystyrene 100 weight section. Since some which carry out fly off have a foaming agent in dehydration, desiccation, and a cool place at the time of aging in order for the above to carry out the amount content of foaming agents into the expandable polystyrene particle at the time of making it foam primarily, this amount of fly off is foreseen and it is necessary to make [many] the amount of impregnation of a foaming agent. moreover, the amount of foaming agents contained in an expandable polystyrene particle -- 0.08-mol % -- under the section -- 100 or more-time expansion ratio -- foaming -- being hard -- since it will stop being able to carry out homogeneity distribution of the foaming agent into polystyrene and will be easy to become the primary foaming particle of the uneven diameter of air bubbles if it increases more than another side and 0.16-mol %, it is not desirable.

[0011] The organic sulfur system compound shown in the expandable polystyrene particle used by this invention by the following general formula (1) [** 5]



(但し、 $20 \geq n \geq 10$ とする。)

For example, it is required to carry out 0.001-0.01 weight section content of dilauryl 3, 3-thio JIPUROPINETO, dimyristyl 3, 3-thio JIPUROPINETO, distearyl 3, 3-thio JIPUROPINETO, etc. to the polystyrene 100 weight section. Although these organic sulfur system compound is generally used as an antioxidant, since it can adjust in the diameter of optimal air bubbles, it can obtain the foaming particle which can foam to altitude primarily and has a specific diameter of air bubbles by this invention by using a **** minute amount together for the above-mentioned foaming agent and this above-mentioned organic sulfur system compound of the amount of specification as a cellular regulator. The obtained primary foaming particle has the outstanding moldability, and can acquire a high-expansion-ratio-foaming object. Moreover, since the organic solvent is not contained in the high foaming particle of this invention, there is no possibility that foaming particles may coalesce in the case of primary foaming.

[0012] Since it is used as a cellular regulator, it becomes the bigger air bubbles under in the 0.001 weight sections than 0.3mm of diameters of average air bubbles which are the upper limit of the diameter of optimal air bubbles and a moldability worsens, the organic sulfur system compound used by this invention is not desirable. On the other hand, if more organic sulfur system compounds than the 0.01 weight section are made to contain, since contraction recovery is not carried out to ***** before contraction, therefore a moldability gets remarkably bad, the primary foaming particle which became finer than 0.05mm of diameters of average air bubbles too much, and could foam to primary expansion ratio only to about at most 160 times, and was obtained is not desirable.

[0013] Moreover, as the addition approach of an organic sulfur system compound, a suspension

polymerization, the approach of adding at the time of nucleus polymerization impregnation, the approach of adding and mixing, in case [in which polystyrene is pelletized in the shape of a particle using an extruder] it carries out extrusion sinking in in the case, etc. can use it preferably, and even if it is a **** minute amount, it can distribute to homogeneity, for example. [0014] When talc which is used from the former as a cellular regulator is used, a **** minute amount, for example, even if it is going to carry out 0.01 weight section addition, make homogeneity distribute the addition, is difficult. Therefore, the primary foaming particle obtained tends to become what produced foaming nonuniformity, and such a primary foaming particle has bad foaming nature. On the other hand, even if it is possible to fuse at low temperature comparatively with about 37 degrees C and the addition is a **** minute amount, in case the organic sulfur system compound 3 used by this invention, for example, dilauryl, and 3-CHIOJIPUROPINETO are pelletized in the shape of a particle using a suspension polymerization, and the time of nucleus polymerization impregnation and an extruder, melting of them can be carried out and homogeneity distribution can be carried out at polystyrene.

[0015] As an approach of foaming to an expandable polystyrene particle primarily 100 to 300 times in this invention, it is 0.4kg/cm² at gage pressure. It is 1.5kg/cm² above. It is necessary to carry out direct heating foaming using the steam of the vapor pressure of the following. For this, vapor pressure is 0.4kg/cm². In the following, it is because 100 or more times takes time amount carrying out high foaming, the amount of fly off of a foaming agent increases during primary foaming as a result, the amount of residual foaming agents contained in the obtained primary foaming particle decreases too much and a moldability worsens. On the other hand, vapor pressure is 1.5kg/cm². Since air bubbles tend to be torn above in the case of primary foaming, the effect becomes [the cellular film] thin in the high foam of polystyrene like especially this application greatly and a primary foaming particle with a good moldability is not obtained, it is not desirable. Moreover, although heating time is chosen according to target expansion ratio, corresponding to the amount of foaming agents contained in fizz styrene resin, in order to prevent the fly off of a foaming agent as much as possible, considering as less than 150 seconds is desirable [heating time].

[0016] Moreover, the amount of foaming agents contained in the polystyrene primary foaming particle which carried out heating foaming excels especially in a moldability and has the desirable primary foaming particle with which are satisfied of becoming 70% or more of the amount of foaming agents contained in the expandable polystyrene particle on the occasion of primary foaming. That is, the amount of easy-volatility foaming agents in the polystyrene particle which foamed in it primarily since the amount of foaming agents contained in an expandable polystyrene particle was 0.08-0.16-mol % to the polystyrene 100 weight section serves as the 0.056-0.16-mol range of %. In order to control the amount of residual easy-volatility foaming agents in a primary form polystyrene particle in this suitable range, it is 0.4kg/cm² at gage pressure. It is 1.5kg/cm² above. It is necessary using the steam of the following to heat directly and to foam.

[0017]

[Example] Next, this invention is explained still more concretely with an example.

When obtaining pearl-like polystyrene according to example 1 suspension polymerization, to the polystyrene 100 weight section, 0.001 weight section addition of dilauryl 3 and 3-thio JIPUROPINETO was carried out as a cellular regulator, and pearl-like polystyrene of 0.5mm of mean diameters was obtained. 0.20 mol % of n pentane was used for this pearl-like polystyrene as a foaming agent, the foaming agent was sunk in at the temperature of 100 degrees C for about 5 hours, and the expandable polystyrene particle containing 0.15 mol % of n pentane was obtained. After dehydrating this expandable polystyrene particle and drying, it riped for about seven days in the heat insulation warehouse, and the expandable polystyrene particle containing 0.11 mol % of n pentane was obtained. Subsequently, the obtained expandable polystyrene particle was made to foam primarily with the vapor pressure (gage pressure) of 0.9kg/cm². Although this primary foaming particle was once contracted and many wrinkles were visually observed on the particle front face, the wrinkle of the grain child front face which carries out natural neglect during about two days was lost, and carried out contraction recovery. The

expansion ratio of this primary foaming particle that carried out contraction recovery, the diameter of average air bubbles, and the foaming agent content were shown in a table 1.

[0018] 300x400x50mm metal mold with a fumarole is filled up with the primary foaming particle which carried out contraction recovery, and it is 1.0kg/cm². Foaming was carried out with vapor pressure (gage pressure), and the moldability was evaluated. The result was shown in a table 1.

[0019]

[A table 1]

一次発泡前の 発泡剤含有量 (モル%)	一次発泡 加熱時間 (秒)	一次発泡粒子 の発泡倍率 (高倍率)	一次発泡粒子 の平均気泡径 (mm)	一次発泡粒子の 含有発泡剤量 (モル%)	成形性	
					融着性	収縮性
0.11	10	100	0.19	0.09	○	○
0.11	20	200	0.25	0.08	○	○
0.11	30	300	0.30	0.08	○	○

(1) The welding nature of a Plastic solid and shrinkage characteristics estimated the moldability.

(2) Assessment of welding nature is not what was left among the fracture surface when tearing a Plastic solid in the interface between foaming particles, and the rate to the total particle number of the particle torn inside the foaming particle made x O and less than 80% of thing for 80% or more of thing.

(3) Contractile assessment made x that to which contraction of the Plastic solid over a metal mold dimension is measured, dimension contraction exceeds 1% or less, O and dimension contraction exceed 1%, and ** and dimension contraction exceed 5% for 5% or less.

[0020] The primary foaming particle was obtained by the same approach as an example 1 except having carried out 0.005 weight section addition of dilauryl 3 and 3-CHIOJIPUROPINETO as an example 2 air-bubbles regulator. Although the obtained primary foaming particle was once contracted and many wrinkles were visually observed on the particle front face, the wrinkle of the grain child front face which carries out natural neglect during about two days was lost, and carried out contraction recovery. The moldability of this primary foaming particle that carried out contraction recovery was evaluated, and that result was shown in a table 2.

[0021]

[A table 2]

一次発泡前の 発泡剤含有量 (モル%)	一次発泡 加熱時間 (秒)	一次発泡粒子 の発泡倍率 (高倍率)	一次発泡粒子 の平均気泡径 (mm)	一次発泡粒子の 含有発泡剤量 (モル%)	成形性	
					融着性	収縮性
0.10	9	100	0.08	0.08	○	○
0.10	28	300	0.14	0.07	○	○

[0022] The primary foaming particle was obtained by the same approach as an example 1 except having carried out 0.015 weight section addition of dilauryl 3 and 3-CHIOJIPUROPINETO as an example of comparison 1 air-bubbles regulator. The obtained primary foaming particle was once contracted and many wrinkles were visually observed on the particle front face. Although natural neglect during about two days was carried out, the wrinkle on the front face of a particle is not lost, but the primary foaming particle which made especially primary foaming heating time 30 seconds had left many wrinkles to the particle front face. Subsequently, the moldability was evaluated and the result was shown in a table 3.

[0023]

[A table 3]

一次発泡前の 発泡剤含有量 (モル%)	一次発泡 加熱時間 (秒)	一次発泡粒子 の発泡倍率 (高倍率)	一次発泡粒子 の平均気泡径 (mm)	一次発泡粒子の 含有発泡剤量 (モル%)	成形性	
					融着性	収縮性
0.10	8	100	0.02	0.08	○	×
0.10	18	160	0.03	0.07	×	×
0.10	30	140	0.03	0.06	×	×

[0024] The primary foaming particle was obtained by the same approach as an example 1 except having not added an example of comparison 2 air-bubbles regulator at all. Although the obtained primary foaming particle was once contracted and many wrinkles were visually observed on the particle front face, the wrinkle of the grain child front face which carries out natural neglect during about two days was lost, and carried out contraction recovery. The moldability of this primary foaming particle that carried out contraction recovery was evaluated, and that result was shown in a table 4.

[0025]

[A table 4]

一次発泡時の 発泡含有量 (モル%)	一次発泡 加熱時間 (秒)	一次発泡粒子 の発泡倍率 (減倍率)	一次発泡粒子 の平均気泡径 (mm)	一次発泡粒子の 含有発泡剤量 (モル%)	成形性	
					膨張性	収縮性
0.11	11	100	0.35	0.09	○	×
0.11	25	200	0.45	0.08	○	×

[0026] The extruder equipped with a nozzle die was used at example 3 head, after having carried out 0.006 weight section addition of distearyl 3 and 3-CHIOJIPUROPINETO as a cellular regulator, extruding in the shape of a strand and carrying out water cooling in in-line one to the polystyrene 100 weight section, it cut, and the pellet type polystyrene particle with a diameter [of 0.9mm] and a die length of 1.0mm was obtained. Butane 0.22 mol % was used for this polystyrene particle as a foaming agent, the foaming agent was sunk in at the temperature of 85 degrees C for about 5 hours, and the expandable polystyrene particle containing butane 0.15 mol % was obtained. When it riped for about five days in the heat insulation warehouse after dehydrating this expandable polystyrene particle and drying, the expandable polystyrene particle containing butane 0.10 mol % was obtained. Vapor pressure (gage pressure) was changed and was made to foam to the obtained expandable polystyrene particle primarily in 0.5-1.2kg/cm². Although the obtained primary foaming particle was once contracted and many wrinkles were visually observed on the particle front face, the wrinkle of the grain child front face which carries out natural neglect during about two days was lost, and carried out contraction recovery. The expansion ratio of this primary foaming particle that carried out contraction recovery, the diameter of average air bubbles, and the foaming agent content were shown in a table 5.

[0027] Subsequently, 300x400x50mm metal mold with a fumarole is filled up with the primary foaming particle which carried out contraction recovery, and it is 1.0kg/cm². Foaming was carried out with vapor pressure (gage pressure), the moldability was evaluated, and the result was shown in a table 5.

[0028]

[A table 5]

一次発泡時の ゲージ圧 (kg/cm ²)	一次発泡 加熱時間 (秒)	一次発泡粒子 の発泡倍率 (減倍率)	一次発泡粒子の 含有発泡剤量 (モル%)	成形性	
				膨張性	収縮性
0.5	60	150	0.10	○	○
0.5	120	300	0.09	○	○
0.8	30	180	0.11	○	○
0.8	60	300	0.10	○	○
1.0	20	200	0.11	○	○
1.0	40	300	0.10	○	○
1.2	30	300	0.10	○	○

[0029] The expandable polystyrene particle obtained in the example 3 of a comparison and the four examples 3 was made to foam primarily with 0.3 and the vapor pressure (gage pressure) of 1.5kg/cm², respectively, and the primary foaming particle was obtained. The obtained primary foaming particle was once contracted and many wrinkles were visually observed on the particle

front face. It is 0.3kg/cm² when natural neglect during about two days is carried out. For the wrinkle on the front face of a particle, the primary foaming particle made to foam primarily with vapor pressure is 1.5kg/cm², although it was lost and contraction recovery was carried out. The primary foaming particle made to foam primarily with vapor pressure became that by which a wrinkle remains in a particle front face a little. Subsequently, the moldability was evaluated and the result was shown in a table 6.

[0030]

[A table 6]

一次発泡時の ゲージ圧 (kg/cm ²)	一次発泡 加熱時間 (秒)	一次発泡粒子 の発泡倍率 (膨倍率)	一次発泡粒子の 含有発泡剤量 (モル%)	成形性	
				融着性	収縮性
0.3	420	150	0.04	×	△
1.5	20	300	0.02	×	×

[0031]

[Effect of the Invention] As stated above, this invention can obtain the polystyrene primary foaming particle which was excellent in the moldability with the thing of 100 to 300 times made to foam primarily highly at the vapor pressure of specific conditions in the expandable polystyrene particle which adjusted the easy-volatility foaming agent of the amount of specification, and the specific cellular regulator to the specific range, and used them together. Since the polystyrene primary foaming particle excellent in this moldability can be easily fabricated to the Plastic solid of 100 to 300 times which carried out altitude foaming, it does so the effectiveness that a foaming object can be acquired efficiently. Moreover, since it can foam to altitude, without using additives, such as an organic solvent, in this invention, there is no possibility that a primary foaming particle may coalesce mutually.

[Translation done.]